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(54) Title: POLY[(R)-3-HYDROXYBUTYRATE] BASED POLYESTER

(57) Abstract

A polyester consisting essentially of poly[(R)-3-hydroxybutyrate] units in which ageing has occurred, characterised in that (i) the polyester is restored to its original non-aged properties by a heat treatment, and (ii) subsequent ageing of the polyester is retarded as indicated by substantial stability of at least one measurement indicative of ageing. The invention also includes a process of de-ageing aged polyester, and shaped polyester articles subjected to the de-ageing process.

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POLY[(R)-3-HYDROXYBUTYRATE] BASED POLYESTER

THIS INVENTION relates to polyester and shaped polyester articles in particular to polyester and such articles restored to their original non-aged properties after ageing has taken place and a process of de-ageing such polyester and articles.

Whereas the polyester poly[(R)-3-hydroxybutyrate] (PHB) when freshly moulded shows ductile behaviour, subsequent ageing seriously embrittles it and hampers its applicability. Within several weeks of storage at room temperature, the tensile modulus doubles, and the elongation at break drops below 10%. A mild de-ageing treatment by the employment of heat up to 70°C results in a slight and temporary improvement in mechanical properties.

It has now been found that such ageing can be reversed by a defined heat treatment and the so-treated polyester and articles are less subject to subsequent ageing.

According to the present invention there is provided a polyester consisting essentially of poly[(R)-3-hydroxybutyrate] units in which ageing has occurred, characterised in that (i) the polyester is restored to its original non-aged properties by a heat treatment, and (ii) subsequent ageing of the polyester is retarded as indicated by substantial stability of at least one measurement indicative of ageing.

According to a further aspect of the invention there is provided a shaped article at least partly made of polyester consisting essentially of poly[(R)-3-hydroxybutyrate] units in which ageing has occurred, characterised in that (i) the shaped article is restored to its original non-aged properties by heating, and (ii) subsequent ageing of the shaped article is retarded as indicated by substantial stability of at least one measurement indicative of ageing.

"At least partly made" means having structural components made of PHB to such an extent that ageing of the PHB components ages the whole article. Thus for example, PHB may be

homogeneously mixed with other biodegradable polymers such as polylactides. In such mixtures the minimum amount of PHB is at least 30% w/w. Also articles having PHB components linked to other components such as razors and toothbrushes, and articles made of a matrix of some other biodegradable (e.g. starch) or non-biodegradeable polymer (e.g. polypropylene) with PHB inclusions, are within the invention. In such mixtures the minimum amount of PHB is at least 30% w/w. Articles made of PHB alone, nucleated or otherwise, benefit most from the invention.

PHB "consisting essentially of" (R)-3-oxybutyrate units includes PHB homopolymer, and PHB copolymers containing up to 1 mol percent of other oxyalkanoate units whether introduced deliberately or not.

"Substantial stability" means that the polyester or article is for practical purposes not defective for brittleness for at least one month after the de-ageing treatment. For example, using the elongation to break measurement, this means a value of not less than 50% of the original non-aged value at one month after the de-ageing treatment when stored at ambient temperature.

Aged polyester or shaped article in the present context means that it has the mechanical properties equivalent to the polyester or article having been stored for 24 hours or more at 20°C. Non-aged polyester or shaped article in the present context means that it has the mechanical properties equivalent to the polyester or shaped article having been freshly processed, i.e mechanical properties equivalent to storage for up to 24 hours at 20°C, preferably storage for up to and including 1 hour at 20°C of having been processed.

The PHB is capable of a relatively high level of crystallinity, for example over 30%, especially 50-90%, in the

absence of plasticiser. It consists of repetitive units of formula I:

$$- O - C_m H_n - CO - \qquad I$$

where m is 3 or 4 and n is 2m or 2m-2. Typically $C_m H_n$ contains 2 carbon atoms in the polymer chain and a C_1 or C_2 side chain on the carbon next to oxygen in the chain. Particular polyesters contain at least 99 mol% of m=3 units, the remainder being m = 4 units or fractional percentages of units having higher values of m. The molecular weight Mw of the PHB is for example from 50000 to 2 x 10^6, especially over 100000.

The PHB can be a product of fermentation, especially of a microbiological process in which a microorganism lays down PHB during growth or is caused to do so by cultivation in starvation of one or more nutrients necessary for cell multiplication. The microorganisms may be wild or mutated or may have the necessary genetic material introduced into it. Alternatively the necessary genetic material may be harboured by an eukaryote, to effect the microbiological process.

Examples of suitable microbiological processes are the following:

for Formula I material with m = 3 or m = partly 3, partly 4 :

EP-A-69497 (Alcaligenes eutrophus)

for Formula I materials with m = 3

US 410533 (A. eutrophus)

EP-A-144017 (A. latus);

The PHB can be extracted from the fermentation product cells by means of an organic solvent, or the cellular protein material may be decomposed leaving microscopic granules of PHB.

Alternately, the PHB can be a product of synthetic chemistry (Bloembergen, S. and Holden, D. A., Macromolecules. 1989, 22, p1656-1663).

The properties of the polyester or article of the present invention can be assessed using the following measurements :

stress-strain curve including calculations of elongation to break, Youngs modulus, and tensile strength; impact testing, for example IZOD; and dynamic mechanical thermal analysis (DMTA). These are all standard methods for testing mechanical properties.

The invention also provides a process of de-aging an aged polyester consisting essentially of poly[(R)-3-hydroxybutyrate] units which comprises heating at a temperature whereby (i) the polyester is restored to its original non-aged properties, and (ii) subsequent ageing of the polyester is retarded as indicated by substantial stability of at least one measurement indicative of ageing.

The invention also extends to shaped articles of the polyester subjected to the above process.

Any one or more of the above-mentioned characterising properties can be used to monitor the progress of the heat treatment. In practice it is often sufficient to test the polyester or article by taking a sample from a batch, cooling it to room temperature and subjecting it to manual flexing. In established manufacturing it is often possible to fix the heating temperature and then adopt a time that is fully adequate and affords a small margin to cover accidental variations.

The heating temperature is preferably in the range from 90°C to 150°C, especially in the range from 100°C to 140°C

The heating time is typically at least a few seconds, preferably from 5 seconds to 20 hours, especially 0.5 min to 14 hours, after the article has reached the intended temperature. The heating time required for optimal effect is dependent on the heating temperature, i.e. the higher the temperature the less time that is required to achieve optimal effect. Also the temperature can be chosen to suit the characteristics of the processing plant and economic requirements.

Heating can be effected in air or oxygen-depleted or

inert gas or in vacuo, or in water or a fluid which does not interfere with the integrity of the polyester, or in a mould. Heat transfer can be by conduction, radiation, convection or resitive heating.

In the accompanying drawings:

Figure 1 shows stress-strain curves at ambient conditions days, (b) treated as in (a) and subsequently heated for 10 h at 100°C, (c) treated as in (b) and stored for another 120 days.

Example 1

Comparison of stress strain behaviour of aged samples and samples de-aged according to the present invention

PHB homopolymer powder ("BIOPOL" from ICI) having Mw 539000, Mw/Mn 3.5 was mixed with 1.0% of boron nitride nucleating agent in a Hobart (RTM) mixer for about 10 min. The mixture was fed to a Betol 2520 (RTM) 25 mm screw extruder operated at maximum 180°C temperature with a screw speed of 100 rpm. The 4 mm strand so produced was crystallised at 60°C in a water bath and granulated. The granules were dried at 40°C for 20 h and injection-moulded into specimen 2 x 5 x 12 mm using a Boy 15S (RTM) machine at a maximum barrel temperature 180°C, injection time 15 sec, screw speed 220 rpm, injection pressure 5MPa, mould temperature 60°C, cooling time 15 sec. The specimens were allowed to age for 150 days at ambient temperature. Then the specimens were subjected to the following treatments :

(a) no further treatment

(b) heated for 10 h at 100°C

(c) treated as in (b) and stored for a further 120 days at ambient temperature.

The three specimens were examined for stress-strain behaviour using an Instron (RTM) 1122 tensile testing machine fitted with a Nene data analysis system. A clamp separation of 50 mm and a crosshead speed of 20 $mm.min^{-1}$ were used. The injection moulded specimens were dumbbell-shaped according to

ISO R 537/2, their prismatic part measuring 40 x 5 x 2 mm.

The variation of percentage extension with applied stress (MPa) is shown in Figure 1. It is evident that, whereas specimen (a) fractured at a stress producing less than 10% strain, specimen (b) demonstrates deaging has taken place as exemplified by the large improvement in the stress-strain relationship. Specimen (c) retained the improved ageing performance for the 120 days further storage. Thus the heat treatment has not only restored the original non-aged properties of the material but has prevented, or at least retarded subsequent ageing.

CLAIMS FOR PCT APPLICATI N

1 A polyester consisting ess ntially of poly[(R)-3-hydroxybutyrate] units in which ageing has occurred, characterised in that (i) the polyester is restored to its original non-aged properties by a heat treatment, and (ii) subsequent ageing of the polyester is retarded as indicated by substantial stability of at least one measurement indicative of ageing.

2 A polyester according to claim 1 wherein the temperature of the treatment is from 90°C to 150°C.

3 A polyester according to claim 1 or 2 wherein the period of heat treatment is from 5 seconds to 20 hours.

4 A polyester according any of claims 1 to 3 in which the poly[(R)-3-hydroxybutyrate] (PHB) is a product of a fermentation process in which a microorganism lays down PHB during growth or is caused to do so by cultivation in starvation of one or more nutrients necessary for cell multiplication.

5 A process of de-aging an aged polyester consisting essentially of poly[(R)-3-hydroxybutyrate] units which comprises heating at a temperature whereby (i) the polyester is restored to its original non-aged properties, and (ii) subsequent ageing of the polyester is retarded as indicated by substantial stability of at least one measurement indicative of ageing.

6 A process according to claim 5 wherein the temperature is in the range from 90°C to 150°C.

7 A process according to claim 5 or 6 wherein the polyester is heated for 5 seconds to 20 hours.

8 A process according to any of claims 5 to 7 in which the poly[(R)-3-hydroxybutyrate] (PHB) is a product of a fermentation process in which a microorganism lays down PHB during growth or is caused to do so by cultivation in starvation of one or more nutrients necessary for cell

multiplication.

9 A process according to any of claims 5 to 8 wherein the polyester is in the form of a shaped article.

10 A shaped article at least partly made of polyester consisting essentially of poly[(R)-3-hydroxybutyrate] units in which ageing has occurred characterised in that (i) the shaped article is restored to its original non-aged properties by a heat treatment, and (ii) subsequent ageing of the shaped article is retarded as indicated by substantial stability of at least one measurement indicative of ageing.

11 A shaped article according to claim 10 wherein the temperature of the heat treatment is from 90°C to 150°C.

12 A shaped article according to claim 10 or 11 wherein the period of the heat treatment is from 0.5 mins to 20 hours.

13 A shaped article according to any of claims 10 to 12 in which the poly[(R)-3-hydroxybutyrate] (PHB) is a product of a fermentation process in which a microorganism lays down PHB during growth or is caused to do so by cultivation in starvation of one or more nutrients necessary for cell multiplication.

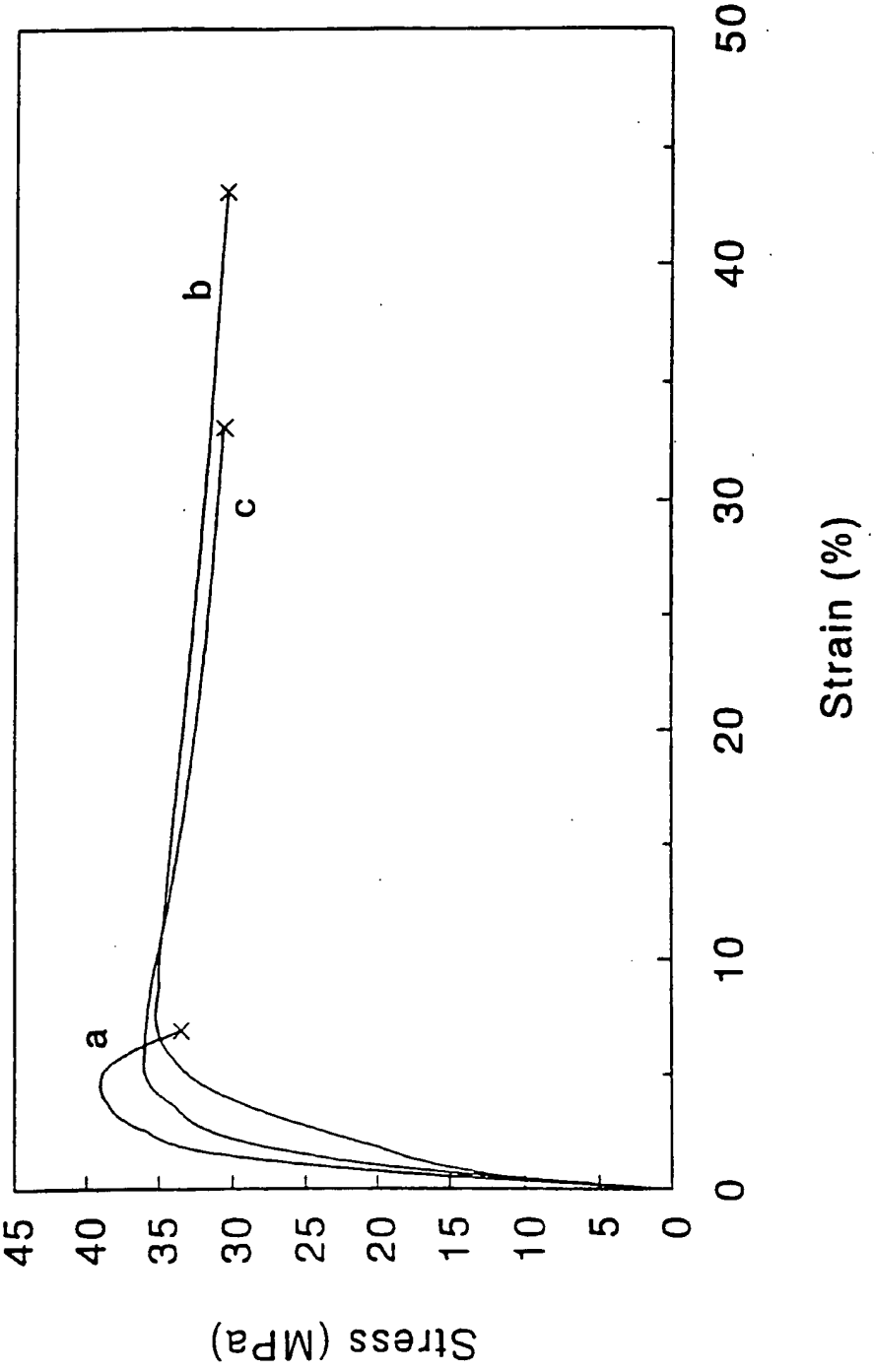

FIGURE 1

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 93/00164

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C08G63/06; C08G63/88; C12P7/62

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C08G ; C12P

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
A	CHEMICAL ABSTRACTS, vol. 117, no. 16, 19 October 1992, Columbus, Ohio, US; abstract no. 151805b, G.J.M. DE KONING; ET AL 'Aging phenomena in bacterial poly((R)-3-hydroxybutyrate). 1. A study on the mobility in poly((R)-3-hydroxybutyrate) powders .gamma.-radiolysis at 77 K' & Polymer, 1992, 33(15), 3295-7 (Eng) see abstract	1-4
A	EP,A,0 104 731 (IMPERIAL CHEMICAL INDUSTRIES PLC) 4 April 1984 see claims	5-13

-/--

° Special categories of cited documents : [10]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
09 AUGUST 1993	18.08.93
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	Kathryn Y.-P. Miao

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	CHEMICAL ABSTRACTS, vol. 110, no. 24, 12 June 1989, Columbus, Ohio, US; abstract no. 213897z, M. SCANDOLA; ET AL 'The physical aging of bacterial poly(D-.beta.-hydroxybutyrate)' & Makromol. Chem., Rapid Commun., 1989, 10(2), 47-50 (Eng) see abstract	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

GB 9300164
SA 69202

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0104731	04-04-84	DE-A- 3374698	07-01-88
		JP-C- 1638983	31-01-92
		JP-B- 2063055	27-12-90
		JP-A- 59059419	05-04-84
		US-A- 4537738	27-08-85